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EFFECT OF AGGREGATE PARTICLE SIZE AND COMPOSITION ON EXPANSION OF MORTAR BARS DUE TO DELAYED ETTRINGITE FORMATION

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ABSTRACT

The effect of aggregate composition and particle size on the expansion of mortar bars, due to delayed ettringite formation (DEF), was evaluated by heat-curing mortar bars made with basalt, dolostone, granite, limestone, siliceous limestone, and pure crystalline quartz. Subsequent to heat curing, the mortar bars were subjected to 3 thermal cycles to accelerate the formation of DEF. They were then stored in lime water for 59 days and length change was monitored. Only mortar bars made with quartz aggregate showed significant expansion. Expansion was found to be inversely proportional to the particle size of the quartz aggregate. The amount of ettringite formed in the mortar bars was shown to be proportional to their rate of expansion. *© 1998 Elsevier Science Ltd*

Introduction

Premature deterioration of steam-cured Portland cement concrete has been attributed to the delayed formation of ettringite (DEF) after the concrete has hardened and been exposed for several years to moist conditions (1–8). The first reactions to occur, when Portland cement concrete is cured under ambient conditions, are associated with tricalcium aluminate (C_3A) and its reaction with sulfates in the pore solution to form ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}2H_2O{\cdot}32H_2O$). In heat-cured concrete, the sulfate, instead of reacting with the aluminate phase, is thought to be adsorbed by the hydrating tricalcium silicate (C_3S) to form the so-called Phase X of Kalousek & Adams (9). In heat-cured concretes/mortars the hydration of C_3S is accelerated.

There is considerable confusion in the literature concerning the use of the terms “delayed” and “secondary” ettringite, and in some instances the two are used interchangeably (10). The term “delayed ettringite” is defined here as ettringite formed, in heat-cured concrete, after it has hardened and has been exposed to moist conditions. Delayed ettringite is thought to form in micro-cracks resulting from the heat treatment of the fresh concrete. Sylla (11) and Fu et al. (12)

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showed that ettringite forming at the crack tips created expansive pressure leading to extension of the cracks. Such ettringite is frequently observed at the paste-aggregate interface (3,5,6,8,12). Lewis et al. (5) showed that no ettringite was present initially in mortar after heat curing, but that it formed subsequently when the mortar was exposed to moisture. Further discussion of the mechanism of delayed ettringite formation lies outside the scope of this paper.

Research by Grabowski et al. (14) and Fu (15) reported that expansion of mortar bars due to delayed ettringite formation was influenced by the composition of the cement and also possibly by the type of aggregate used.

The purpose of this investigation is to determine the effect of aggregate type and particle size on expansion of mortar bars due to delayed ettringite formation (DEF). There is currently no universal or standardized method of testing cement-aggregate combinations for premature deterioration due to delayed ettringite formation. Heinz & Ludwig (1) developed a test using mortar bars heat-cured to temperatures varying from 75°C to 100°C. No expansion was observed at 75°C; maximum expansion was observed at 100°C. The disadvantage of this test is that some samples did not start expanding until after one year of storage in water at 20°C.

Grabowski et al. (14), used the “Duggan Test” to evaluate the effect of aggregate and cement composition on deterioration of concrete due to ettringite formation resulting from heat treatment. In this test, concrete is cast and hydrated under ambient conditions. Cores are taken from the hardened concrete, which are then subjected to three cycles of dry heat at 82°C, followed by cooling in distilled water at 21°C, i.e., the “Duggan Cycle.” Subsequently the cores are stored in distilled water and length change is monitored for 90 days. This test method does not evaluate deterioration due to DEF because ettringite would have formed in the normal way when the concrete was cured under ambient conditions. Following the Duggan Cycle, the early formed ettringite or monosulfoaluminate goes into solution and is re-precipitated as secondary ettringite in cracks formed by thermal cycling.

Fu (15) developed a test method for “stability of Portland cement mortars moist-cured at high temperatures,” which was proposed as an ASTM test. The mortar bars are prepared using silica sand and Portland cement, with a cement/sand ratio of 0.36 and a w/c of 0.48. The specimens are cured for 1 h in a fog room at 23°C. The molds containing the mortar bars are then heated at 95°C for 12 h and cooled to ambient temperature over a period of 4 h. The mortar bars are then demolded and stored in water for 6 h at 23°C before taking the zero length reading. The samples are then stored in lime water at 23°C, and the length is monitored for 56 days. This method appears to be the most practical of the methods proposed. However, it has not yet been demonstrated that cements causing expansion in the accelerated test would in fact cause deleterious expansion in incorrectly steam-cured field concrete.

The accelerated test developed by Fu was selected for this investigation. The reasons for this selection are that it appears be the most rapid of the proposed methods, and that it will extend the investigations commenced by Fu.

Experimental Materials

Cement

In the experiments designed to investigate the effect of aggregate composition and particle size on expansion due to DEF, a CSA Type 30 (16) (ASTM Type III) cement (Table 1) was used. This cement was selected because it gave maximum expansion in earlier tests (15).

TABLE 1
Composition of the Type 30 cement.

Cement	Fineness cm^2/g	Mineralogical Composition % C_3S	C_2S	C_3A	C_4AF
Type30#1	5682	54.21	16.07	10.26	5.81

Oxide composition (mass %)

SiO_2	Al_2O_3	CaO	Fe_3O_3	MgO	Na_2O K_2O	SO_3	LOI
19.87	5.09	62.34	1.91	2.98	0.60	4.08	2.48

Fine Aggregates

In all the mixtures, except those designed to investigate the effect of particle size on expansion due to DEF, were graded as shown in Table 2. A pure quartz sand mixed with crushed crystal quartz was used in all experiments except those designed to investigate the effect of aggregate composition on expansion due to DEF. In the latter the following rock types were used: basalt, dolostone, granite, non-reactive limestone, reactive limestone, and quartz. (The reactive limestone is a well-documented alkali-silica reactive limestone from Ottawa ON, Canada (Spratt limestone).)

In the experiments made to evaluate the effect of particle size of quartz aggregate on expansion, four size fractions, one for each mixture were used: −5.00 + 2.5 mm; −2.5 + 1.25 mm; −1.25 + 630 μm; and −630 + 315 μm.

Mixing of Mortar

The mortars were mixed according to ASTM C 305, except that in the case of the mixtures containing only the coarse fractions of quartz, some modification was required. A minimum of 4 mortar bars 25.4 × 25.4 × 152 mm were made from each mixture. The quantities of materials used to prepare 4 mortar bars were 500 g cement, 1375 g graded fine aggregate, and 240 mL water.

TABLE 2
Aggregate grading.

Sieve sizes	percent retained	weight (g)
−5.00 + 2.50 mm	10	82.5
−2.5 + 1.25 mm	10	82.5
−1.25 + 630 μm	30	247.5
−630 + 315 μm	40	330.0
Pan size	10	82.5
Total	100	825.0

Curing

The curing cycle followed was that proposed by Fu (16). After filling the molds, they were placed in a fog room at 23°C for 1 h. The molds were then transferred to sealed containers and placed in an oven. The heaters were turned on. A high rate of heating was used so that the temperature rose to 95°C in 1 h. The samples were maintained at 95°C for 12 h when the heaters were turned off and the oven allowed to cool for 4 h. The mortar bars were then demolded and placed in lime water at 23°C for 6 h prior to measuring the initial lengths.

Thermal Cycling

Following the initial length measurement, the samples were placed in an oven at 85°C for 24 h. After cooling, the samples were again immersed in lime water for 24 h. This constitutes one thermal cycle. The samples were then subjected to a total of 3 thermal cycles in order to accelerate expansion during subsequent storage in lime water at 23°C. Length change was monitored for a minimum of 56 days.

Results

Effect of Aggregate Composition on Expansion

The expansions obtained from the mortar bars containing 6 rock/mineral types are shown in Figure 1a. Expansion greater than 0.1% at 56 days was only observed in the mortar containing quartz aggregate. X-ray diffraction analysis (Fig. 1b) showed that the mortar made with quartz aggregate contains more ettringite than the limestone mortar.

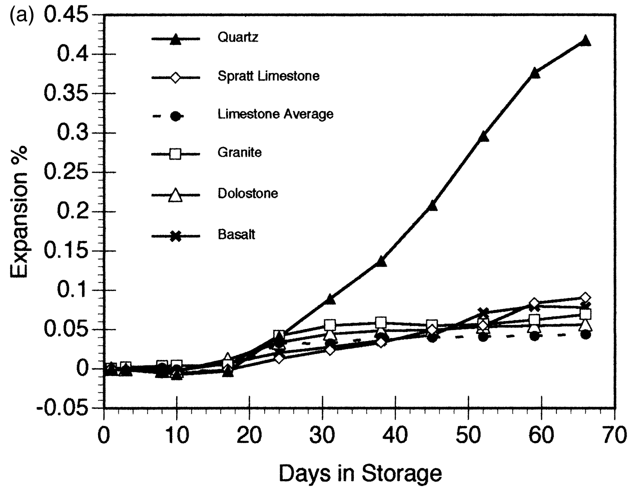
Effect of Aggregate Particle Size on Expansion

The rate of expansion of mortar contining quartz with varying particle size was calculated from a plot of expansion vs. the square root of time in days by fitting a line to the linear part of the expansion curve and determining its slope. It was found to be inversely proportional to the particle size as shown in Figure 2. It is also evident from Figure 2 that the rate of expansion is related to the surface area of the aggregate.

Discussion

Effect of Aggregate Composition

The observation of ettringite at the paste aggregate interfaces (Fig. 3) in laboratory heat-cured mortar or field concretes showing significant expansion due to DEF is a good indication that the aggregate surface has a significant role in the deterioration process. It is therefore not too surprising that expansion is proportional to the surface area of the aggregate, as was observed in this investigation (Fig. 2).



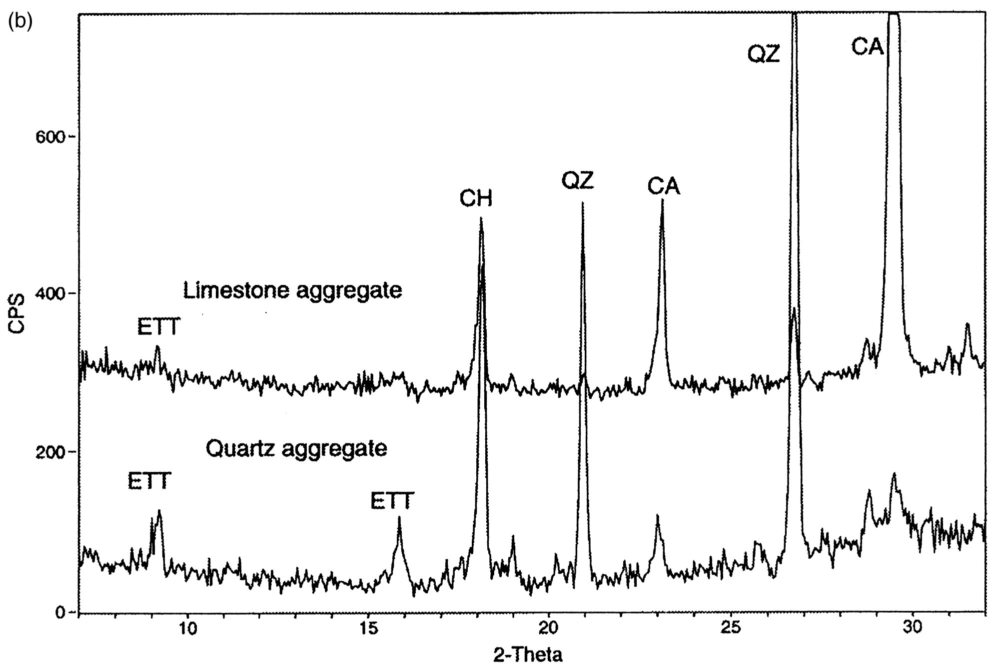


FIG. 1.

a) Efect of aggregate composition on expansion due to DEF. *b*) X-Ray diffractogram showing the ettringite peaks in the mortar bars made with quartz and limestone aggregates. ETT, ettringite; QZ, quartz; CA, calcite.

The results of the experiments designed to evaluate the effect of aggregate composition on expansion due to DEF are surprising. Only the mortar containing quartz expanded (Fig. 1a). Evaluation of deteriorated rail ties from both in Canada and USA by the first author (unpublished results) showed that ettringite deposits similar to what was observed in the quartz mortar bars were found in concretes made with granite-gneiss and limestone aggre-

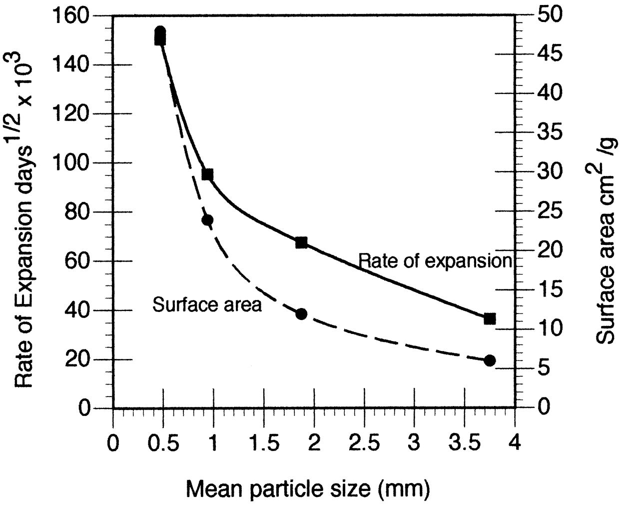


FIG. 2.
Correlation between inverse of the particle size and surface area of quartz aggregate and the rate of expansion of mortar bars.

gates. However, in many if not all reported cases, the initial cracking may have been caused by alkali-silica reaction (19,20), and the ettringite may be at least partly secondary rather than DEF. Furthermore, if the inverse relationship between aggregate particle size and expansion observed in this investigation holds in field concretes, the coarse aggregate may not have a significant role in expansion and deterioration due to DEF.

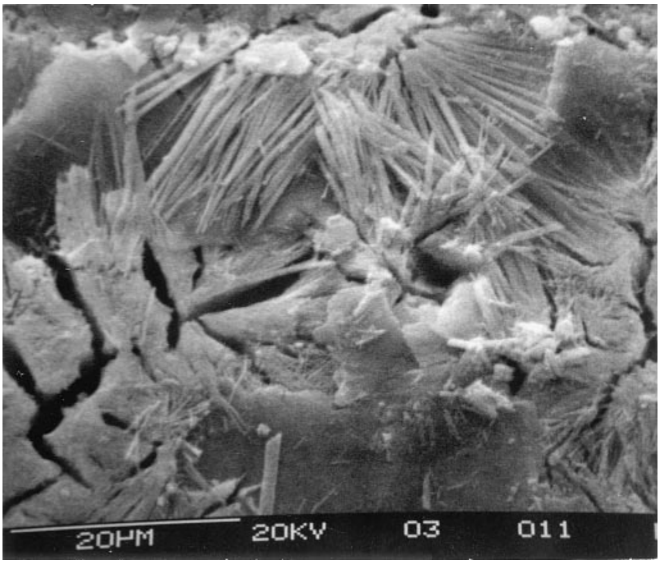


FIG. 3.
SEM micrograph of an aggregate/paste interface showing a coating of ettringite exhibiting the characteristic shrinkage cracks.

The mortar bars made with quartz aggregate, in addition to showing greater expansion than those made with other types of aggregate, also contained more ettringite as shown by X-ray diffraction (Fig. 1b). The quartz mortar was quite weak after 205 days' storage in lime water, and the aggregate was readily separated for examination of the paste-aggregate interfaces, many of which were coated by ettringite (Fig. 3). By comparison, the limestone mortar was hard and separation of aggregate particles from the paste difficult. It is not known if steam-cured concrete made with limestone, granite, and basalt aggregates would also show minimal expansion and cracking. A lengthy field investigation would be necessary to determine this.

The dolostone mortar showed about the mean expansion 0.056% of the non-quartz aggregate mortars. The range of expansions of these mortar bars is from 0.84% for the reactive limestone to 0.04% for the non-reactive limestone. The range of expansions amongst the mortar bars without quartz is about the same as the scatter between the 4 individual mortar bars made with dolostone aggregate, as expressed by 3 standard deviations from the mean ($\pm$0.025%). This suggests that the differences in expansions between the non-quartz mortar bars are not significant.

Initially, it was thought that differences in the coefficient of thermal expansion between the aggregate and the cement paste (coefficient of thermal expansion of paste $\sim 13 \times 10^{-6}$/°C) might be responsible for microcracking the mortar during the heat curing cycles. However, this hypothesis was discarded because the maximum difference in thermal expansions occurs with limestone, with a coefficient of thermal expansion of $\sim 5 \times 10^{-6}$/°C. The limestone mortar showed minimum expansion due to DEF.

A review of the literature showed that because aggregate comprises about 70% of mortar/concrete the coefficient of thermal expansion of concrete is largely determined by that of the aggregate (21). The thermal coefficients of agregates vary from a low of about 6×10^{-6}/°C for limestone to about 10×10^{-6}/°C for quartz. Walker et al. (21) showed that the number of heating/cooling cycles (from 4.4 to 60°C) required to reduce the modulus of rupture of concrete by 75% was proportional to the coefficient of thermal expansion of the concrete (Fig. 4). The rate of expansion of the DEF mortar bars is plotted against the coefficient of thermal expansion of the aggregate used in Figure 5. From this figure, it is evident that high rates of expansion are only observed when the thermal coefficient of expansion of the aggregate is greater than about 10×10^{-6}/°C. In the present experiments, the mortar bars were heated through a range of 70°C. The strain caused by heating the mortar through 70°C is shown along the top of the graph (Fig. 5). In concrete or mortar, expansions of over $\sim$400 microstrain (0.04%) due to alkali-silica or alkali carbonate reactions generally cause visible cracks on the test prisms or bars. Presumably, at this amount of expansion, the tensile strength of the material is exceeded, leading to the formation of cracks. It would appear from Figure 5 that in DEF mortar bars expansions greater than about 650 microstrain create microcracks, providing a site for the crystallization of ettringite (12). This amount of expansion is not too different from that required to cause cracking due to alkali aggregate reaction (AAR). The difference may be due to the stress being continuous in AAR, while it is only temporarily applied during thermal curing of the mortar bars. It would appear from the results of this investigation that it is the composition of the fine aggregate which determines to potential for DEF in heat-cured concrete made with Type III cements. The role of coarse aggregate on DEF, if any, was not investigated in this study. A long-term series of tests using concrete prisms would be necessary to evaluate the effect of coarse aggregate on DEF.

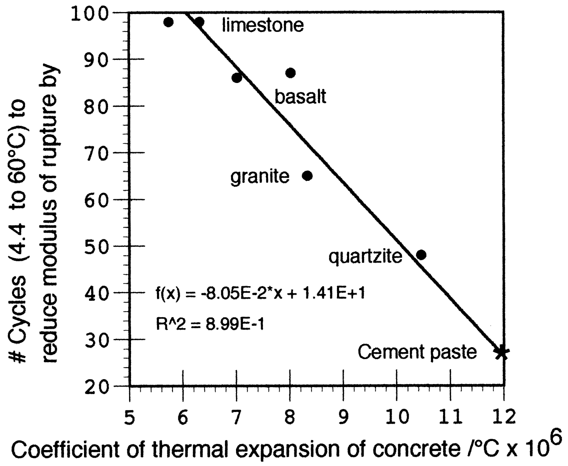


FIG. 4.

Effect of aggregate type on coefficient of thermal expansion and on the number of heating/cooling cycles required to reduce the modulus of rupture by 75% (21).

Effect of Aggregate Particle Size on Expansion

It is evident from Figure 2 that expansion depends on the surface area of the aggregate. Both surface area and the rate of expansion show a marked increase at particle sizes less than 1 mm. The intensity of the 0.560 nm peak at 15.85° 2θ in the X-ray diffractograms was used as a measure of the amount of ettringite in the mortar bars. The intensity of the 0.560 nm peak

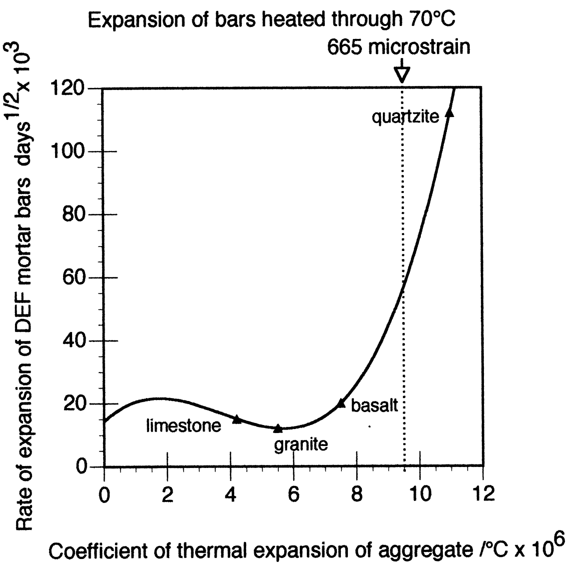


FIG. 5.

Effect of thermal coefficient of expansion of aggregate on the rate of expansion of mortar bars due to DEF.

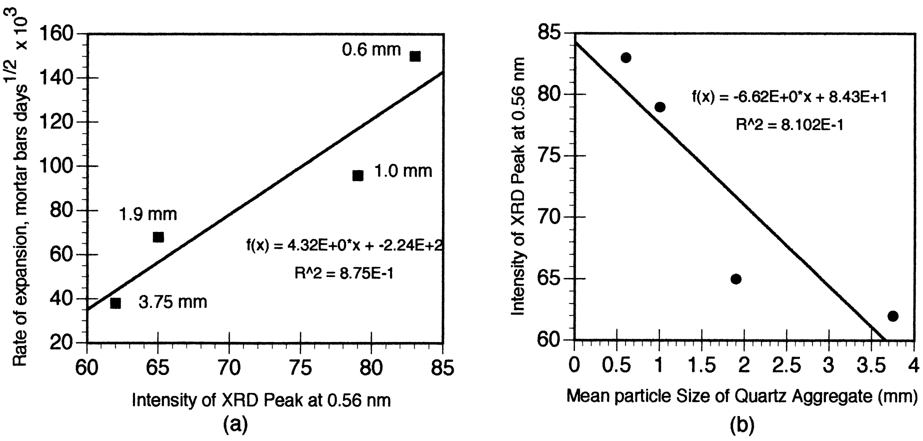


FIG. 6.

a) Correlation between the intensity of the XRD peak due to ettringite at 0.560 nm and the rate of expansion of mortar bars. *b*) Correlation between the intensity of the XRD peak due to ettringite at 0.560 nm and the mean particle size of the quartz aggregate in the mortar bars.

is shown plotted against the expansion of the DEF mortar bars in Figure 6a. It is concluded from this figure that expansion is proportional to the amount of ettringite formed in the mortar bars. Figure 6b shows the correlation between the intensity of the 0.560 nm peak and the mean particle size of the quartz aggregate.

Although the correlation is not very good, the intensity of the XRD 0.560 nm peak increases with fineness of the quartz aggregate in the mortar bars, indicating that the amount of ettringite increases with diminishing aggregate particle size. These results suggest that it is the finer fractions of the fine aggregate which determine the amount of ettringite formed and the amount of expansion in heat-cured mortar bars.

Conclusions

1. The composition of the fine aggregate was shown to have a marked effect on the amount of ettringite formed and on expansion, due to DEF of heat-cured mortar bars.
2. Aggregate with a coefficient of thermal expansion of greater than about 10×10^{-6}/°C caused sufficient expansion of the mortar bars during the thermal cycling to create a pattern of microcracks and sites for the crystallization of ettringite. Of the aggregates tested, only quartz, with a thermal coefficient of expansion of $\sim 11 \times 10^{-6}$/°C, caused significant expansion of the DEF mortar bars.
3. It is not known at present what effect, if any, the coarse aggregate in concrete has on the expansion due to DEF in heat-cured concrete.
4. Expansion and the amount of ettringite formed in heat-cured mortar bars is inversely proportional to the grain size of the quartz aggregate. The rate of expansion increased rapidly as the mean particle size decreased below 1 mm.
5. Long-term tests using concrete prisms are needed to confirm that the above results apply to heat-cured field concretes.

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